

## Ancient starch: Cooked or just old?

Henry et al. (1) argued for greater sophistication in Neanderthal diets on the basis of the identification of ancient starch granules, some of which—according to changes in morphology—displayed “clear evidence of cooking.” Despite the emphasis on morphology and morphological change, there is no attempt to apply any statistical rigor to their morphology-based identifications (cf. ref. 2); nor is there any attempt to independently confirm that any of the observed structures are indeed composed of starch. Biochemical tests, such as digestion with *Bacillus licheniformis* 1,4- $\alpha$ -D-glucan-glucanohydrolase (3), can confirm the presence of starch and may give some insight into diagenesis. Similar characterization of other ancient biomolecules (proteins, lipids, lignocellulose, and DNA) has revealed a general truth that the older a sample is, the more degraded it is. The authors do consider that chewing may have altered the morphology of some granules (their Supporting Information) but do not consider a more prosaic explanation—namely that granules were not cooked, but merely old.

There exists an extensive literature on the rates of starch degradation below the gelatinization point (i.e., starch diagenesis). Limited starch swelling and internal chain transitions will first result in some disruption of granule morphology without loss of birefringence (4); ultimately the granules will gelatinize. If typical kinetics parameters for low-temperature starch gelatinization are used to estimate survival at burial temperatures (Ea 332 kJ mol<sup>-1</sup>, A 7.20  $\times$  10<sup>48</sup>; e.g., table 3 of ref. 5), then half the granules would be expected to have gelatinized in less than 500 y at 20 °C; the same process would take  $\approx$ 100 times longer at 10 °C. The finding that there is more evidence of “cooked” granules at Shanidar than at Spy is not unexpected. Using comparative estimates of the temperature histories at both sites and the dates given in the article, starch granules will take 2 to 100 times longer to gelatinize at Shanidar than at Spy. The wide error margin on estimates arises owing to the magnification

of subtle differences in the estimated thermal history arising from the high activation energy of starch gelatinization. The fact that grass seed starch was “cooked,” whereas other granules were not damaged, is probably attributable to the wide variety of activation energies reported for starch gelatinization (5).

Despite the growing interest in the analysis of ancient starch granules, studies of diagenesis are rare. Because of the sensitivity to temperature and hydration of low-temperature gelatinization, as well as the variability between different starch types, starch diagenesis arguably needs to be studied with greater rigor than has been applied to other ancient macromolecules. This is particularly true when granules are identified in sites with high thermal ages, or if some form of thermal processing is being claimed (1). Bone collagen progressively also gelatinizes during cooking, but differences in collagen levels between Neanderthal sites in Iraq and Belgium are usually attributed to diagenetic causes.

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1. Henry AG, Brooks AS, Piperno DR (2011) Microfossils in calculus demonstrate consumption of plants and cooked foods in Neanderthal diets (Shanidar III, Iraq; Spy I and II, Belgium). *Proc Natl Acad Sci USA* 108:486–491.
2. MacLeod N, O'Neill M, Walsh SA (2007) A comparison between morphometric and artificial neural net approaches to the automated species-recognition problem in systematics. *Biodiversity Databases: From Cottage Industry to Industrial Network*, eds Curry G, Humphries C (CRC Press, Boca Raton, FL), pp 37–62.
3. Hardy K, et al. (2009) Starch granules, dental calculus and new perspectives on ancient diet. *J Archaeol Sci* 36:248–255.
4. Saibene D, Seetharaman K (2006) Segmental mobility of polymers in starch granules at low moisture contents. *Carbohydr Polym* 64:539–547.
5. Sablani SS, et al. (2007) Isobaric and isothermal kinetics of gelatinization of waxy maize starch. *J Food Eng* 82:443–449.

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